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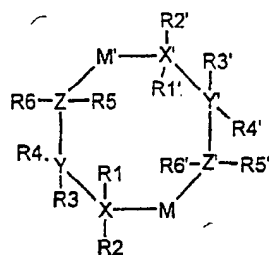
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(54) Volatile precursors for deposition of metals and metal-containing films

(57) This invention is directed to a group of novel homologous eight membered ring compounds having a metal, such as copper, reversibly bound in the ring and containing carbon, nitrogen, silicon and/or other metals. A structural representation of the compounds of this invention is shown below:



wherein M and M' are each a metal such as Cu, Ag, Au and Ir; X and X' can be N or O; Y and Y' can be Si, C, Sn, Ge, or B; and Z and Z' can be C, N, or O. Substituents represented by R1, R2, R3, R4, R5, R6, R1', R2', R3', R4', R5', and R6' will vary depending on the ring atom to which they are attached. This invention is also directed to depositing metal and metal-containing films on a substrate, under ALD or CVD conditions, using the above novel compounds as precursors.

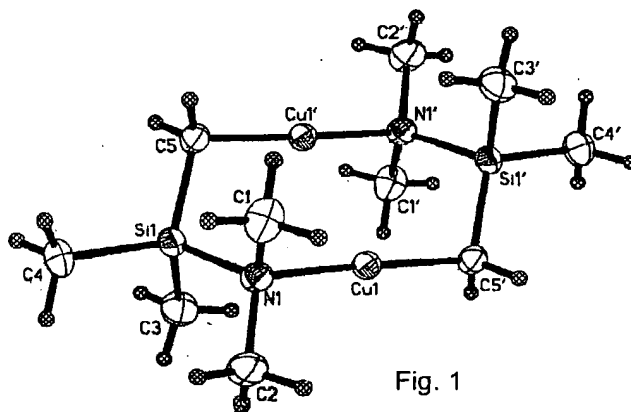


Fig. 1

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Description

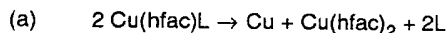
BACKGROUND OF THE INVENTION

[0001] The semiconductor industry is now using copper interconnects in state of the art microprocessors. These embedded fine metal lines form the three dimensional grid upon which millions of transistors at the heart of the microprocessor can communicate and perform complex calculations. Copper is chosen over the more conventionally used aluminum since it is a superior electrical conductor thereby providing higher speed interconnections of greater current carrying capability. These interconnect pathways are prepared by the damascene process whereby photolithographically patterned and etched trenches (and vias) in the dielectric insulator are coated with a conformal thin layer of a diffusion barrier material (for copper this is usually tantalum or tantalum nitride) and then completely filling in the features with pure copper. Excess copper is then removed by the process of chemical mechanical polishing. Since the smallest features to be filled can be less than 0.2 microns wide and over 1 micron deep, it is crucial that the copper metallization technique used is capable of evenly filling these deeply etched features without leaving any voids which could lead to electrical failures in the finished product. Copper chemical vapor deposition (CVD) is a technique that is well known for its ability to 'gap fill' such structures. In this process, a vapor of a volatile organometallic species containing copper is introduced to the surface to be metallized, whereupon a chemical reaction occurs in which only copper is deposited on the surface. Since the copper is delivered in a vapor form it evenly accesses both vertical and horizontal surfaces to yield a very evenly distributed film. Many precursors for copper CVD are known. The most desirable are those that are highly volatile, give pure copper films and do not introduce contaminating species into the reaction chamber or onto diffusion barrier surfaces. Currently, the biggest challenge facing copper CVD is its poor adhesion to tantalum-based diffusion barriers leading to delamination of the copper film during chemical mechanical polishing.

[0002] CVD copper precursors can be grouped into the following three major categories:

1. CVD copper using $\text{Cu}(\text{hfac})\text{L}$ type precursors where (hfac) represents 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion and (L) represents a neutral stabilizing ligand, usually an olefin an alkyne or a trialkylphosphine.

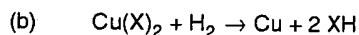
Many of these compounds are volatile liquids, the most well known being the compound $\text{Cu}(\text{hfac})\text{tmvs}$, where tmvs is trimethylvinylsilane, known commercially as CupraSelect®, available from Schumacher unit of Air Products and Chemicals, Inc., and described in U.S. Patent No. 5,144,049. This class of precursors function by a process of disproportionation, whereby two molecules of $\text{Cu}(\text{hfac})\text{L}$ react together on a heated substrate surface to give copper metal, two molecules of free ligand (L) and the volatile by-product $\text{Cu}(\text{hfac})_2$. This is shown below in Equation (a):



This process is typically run at around 200 °C. Note that in this process one half of the copper from the initial precursor cannot be utilized since it constitutes part of the $\text{Cu}(\text{hfac})_2$ by-product. One potential drawback of these precursors is their tendency to chemically degrade upon contact with tantalum or tantalum nitride diffusion barrier surfaces before the CVD copper film can begin to form. The chemical cause of this adverse reaction is thought to stem from the fluorocarbon character of the 'hfac' portion of the copper precursor rendering it reactive with tantalum. This degradation leads to a thin layer of chemical debris forming between the tantalum and copper. The lack of direct contact between the tantalum and copper is thought to cause three main effects. First, the mechanical adhesion between the two metals is compromised, resulting in their tendency for copper to delaminate under conditions of chemical mechanical polishing. Secondly, the chemical debris tends to act as an electrical insulator, resulting in poor electrical contact between the copper and the tantalum. Thirdly, since the copper is not growing directly onto the tantalum, it cannot replicate its crystal orientation, and hence, grows as a randomly oriented film (R. Kroger et al, *Journal of the Electrochemical Society*, Vol.146, (9), pages 3248-3254 (1999)).

2. CVD copper from $\text{Cu}^{+2}(\text{X})_2$

These compounds typically do not give pure copper films by CVD unless a chemical reducing agent, such as hydrogen, is used in the CVD processing, as shown below in Equation (b):

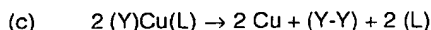


Examples of this type of precursor include; Cu^{+2} bis(β -diketonates) (Wong, V., et al, Materials Research Society Symp Proc, Pittsburgh, PA, 1990, pages 351-57; Awaya, N., *Journal of Electronic Materials*, Vol 21, No 10, pages 959-964, 1992), Cu^{+2} bis(β -diimine) and Cu^{+2} bis(β -ketoimine) compounds (U.S. Patent No. 3,356,527, Fine, S.

M., *Mater. Res. Soc. Symp. Proc.*, 1990, pages 204, 415). These copper⁽⁺²⁾ compounds are typically solids, and the CVD processing temperatures for them are typically above 200 °C. If these precursors are substantially fluorinated, then similar problems with adhesion, etc., are anticipated, as observed for the Cu(hfac)L compounds mentioned above.

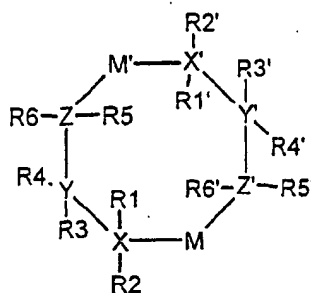
3. CVD copper from (Y)Cu(L) compounds.

In these Cu(+1) precursors, (Y) is an organic anion and (L) is a neutral stabilizing ligand, such as trialkylphosphine. An example of such a precursor is CpCuPEt₃, where Cp is cyclopentadienyl and PEt₃ is triethylphosphine (Beech et al., *Chem. Mater.* (2), pages 216-219 (1990)). Under CVD conditions, two of these precursor molecules react on the wafer surface in a process whereby the two stabilizing trialkylphosphine ligands become disassociated from the copper centers, the two (Y) ligands become coupled together and the copper (+1) centers are reduced to copper metal. The overall reaction is shown below in Equation (c). However, this type of chemistry poses problems in a manufacturing environment, since the released trialkylphosphine ligands tend to contaminate the CVD chamber and can act as undesired N-type silicon dopants.



BRIEF SUMMARY OF THE INVENTION

[0003] The present invention is directed to a group of novel homologous eight membered ring compounds having a metal, such as copper, reversibly bound in the ring and containing carbon, nitrogen, silicon and/or other metals. A structural representation of the compounds of this invention is shown below [1]:



[1]

wherein M and M' are each a metal, such as Cu, Ag, Au, and Ir; X and X' can be N or O; Y and Y' can be Si, C, Sn, Ge, or B; and Z and Z' can be C, N, or O. Substituents represented by R1, R2, R3, R4, R5, R6, R1', R2', R3', R4', R5', and R6' will vary depending on the ring atom to which they are attached. For example, R1, R2, R1', and R2' can each independently be an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, or a fluoroalkyl-substituted aryl; R3, R4, R3', and R4' can each be independently an alkyl, a partially fluorinated alkyl, a trialkyl siloxy, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, an alkoxy, or a halogen; and each of R5, R6, R5', and R6' can each be independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, a halogen, a trialkylsilyl, a triarylsilyl, a trialkylsilanoate, a trialkylsilylamido, or an alkoxy; provided that when X and X' are each O, there is no substitution at R2 and R2'; further provided that when Z and Z' are each O, there is no substitution at R5, R6, R5', or R6'. Alkyl and alkoxy each have 1 to 8 carbons; alkenyl and alkynyl each have 2 to 8 carbons; and aryl has 6 carbons.

[0004] A linear representation of one embodiment of the novel compounds of this invention is [-CuNMe₂SiMe₂CH₂CuNMe₂SiMe₂CH₂-] in which, according to structure [1] above, M and M' are each Cu; X and X' are each N; Y and Y' are each Si; Z and Z' are each C; R1, R2, R3, R4, R1', R2', R3', and R4' are each methyl; and R5, R6, R5', and R6' are each H.

[0005] The compounds of this invention have the remarkable capability of depositing two metal atoms per molecule under chemical vapor deposition conditions by the process of thermal ligand coupling along with simultaneous reduction of the copper centers to copper metal. They are also well suited for use in Atomic Layer Deposition (ALD) of metal or oxide thin films, preferably copper or copper oxide films.

[0006] This invention is also directed to depositing metal and metal-containing films on a substrate, under ALD or

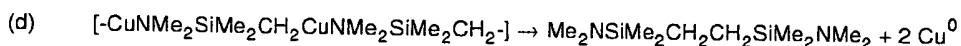
CVD conditions, using the above novel compounds as precursors.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0007] Fig. 1 presents a single crystal X-ray structure of one compound of this invention.

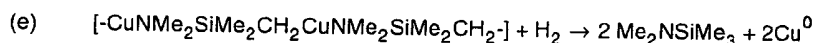
DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention describes a new family of volatile cyclic bimetallic metal precursors, that contain either no fluorine, or low levels of fluorine, relative to the (hfac) ligand described above, or other fluorocarbon bearing ligands, and as such, are expected to provide copper CVD films with excellent adhesion to tantalum barriers. Being cyclic binuclear species, each molecule of precursor contains two ligands, that can reductively couple together and in the process release two atoms of metal. Using copper as an example, metallization has the potential to proceed via intramolecular reductive elimination, as shown below in equation (d) for the binuclear complex $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$, rather than the more common intermolecular reductive elimination shown above in equation (c).



In the equation (c), two molecules of precursor need to interact on a substrate for the reductive coupling and copper nucleation to occur. The kinetic barrier for that process is expected to result in a slower rate of copper nucleation, when compared to the precursors of the present invention. While not wishing to be bound by theory, the net result should be a faster rate of nucleation for the bimetallic precursors of this invention which allows less time for other undesired reactions with the substrate to occur.

[0009] CVD copper can also be formed from these complexes using direct chemical reduction of the complex using a suitable volatile reducing agent such as a silane, borane, hydrazine etc or hydrogen either as a simple gas or as a direct or remote plasma to release, as volatile species, the ligands coordinated to copper while simultaneously reducing the copper (+1) centers to copper metal. This is illustrated below in equation (e) for the hydrogen reduction of the binuclear complex $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ to release dimethylaminotrimethylsilane and copper metal.



[0010] In addition, this new class of binuclear metal complexes are anticipated to be excellent precursors for ALD (Atomic Layer Deposition) growth of metal or metal-containing films.

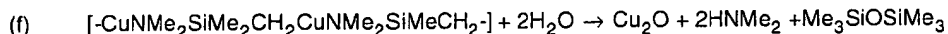
[0011] In ALD the precursor is chemisorbed onto a substrate to form a 'monolayer' of precursor, i.e., one molecule thick. A second reagent species is then similarly introduced to chemically react with the first chemisorbed layer to grow the desired film onto the substrate surface. For example, aluminum oxide can be grown by the ALD process (Higashi, G.S., et al, *Appl. Phys. Lett.*, 55(19) (1989) page 1963; Georghe S.M., et al, *Int. Symp. On Atomic Layer Epitaxy and Related Surface Processes (ALE-3) Abstracts*, Sendai, Japan, 2527 May (1994) page 38) by first exposing a substrate bearing surface OH groups to trimethylaluminum vapor to form a chemisorbed monolayer that contains Al-O and residual Al-CH₃ bonds and then secondly to water vapor. The water vapor reacts with the residual Al-CH₃ groups to give solid aluminum oxide and methane gas, the latter being exhausted from the ALD chamber as a volatile byproduct. Since the water vapor is added in excess, each aluminum atom in the newly formed aluminum oxide surface becomes functionalized with an OH group. This creates a highly reactive surface for the next pulse of trimethyl aluminum vapor to chemisorb onto, again releasing methane in the process. This cycle is then repeated to grow a perfectly conformal and pure film of aluminum oxide whose thickness is determined by the number of cycles run. Precursors that are best suited to ALD are readily volatile, have high chemical reactivity permitting their ligands to be readily removed by the addition of specific reagents and, at the molecular level, are dense in the element to be deposited (reacted) onto the substrate surface. A high ratio of the latter element to its supporting ligands translates to a high effective loading of the element per chemisorbed monolayer and hence to a higher ALD growth rate.

[0012] The binuclear metal complexes described in this disclosure are highly suitable for ALD since they are highly volatile, are very reactive at low processing temperatures towards loss of their ligands to form a metal-containing film and being binuclear they bear two metal atoms per molecule of precursor in the chemisorbed layer.

[0013] ALD copper using copper(+1) chloride (Martensson, P., et al, *Chem Vap Deposition*, 1997, Vol.3, No. 1, page 45) suffers the disadvantage of low volatility of the precursor, ALD copper from copper(+2) bis(tetramethylheptanedi-

onate) (Martensson, P., et al, *J. Electrochem. Soc.*, Vol 145, No 8, August 1998, pages 2926-2931 suffers from the precursor being bulky and mononuclear in copper, and ALD copper using copper⁽⁺²⁾(hfac)₂ (Solanki, R., et al, *Electrochemical and Solid State Letters*, Vol. 3 (10) pages 479-480 (2000)) suffers from the disadvantages of being mononuclear and highly fluorinated.

[0014] The complexes described in this disclosure are highly suitable for the ALD growth of copper and other metals, copper alloys, and copper containing films such as copper sulfide, copper oxide, etc. These films are created by reacting the monolayers of precursor in the ALD technique by thermal processing or chemical reduction, by treatment with other metal compounds or by processing with sulfur or oxygen containing reagents respectively. This disclosure also teaches a superior process for growing copper films by ALD whereby the chemisorbed monolayer of precursor is reacted with water vapor or water vapor plus an oxidant in ALD type cycles to form an ultra thin film of copper oxide. This copper oxide is then reduced by hydrogen gas, remote hydrogen plasma or other suitable reductant, to form copper metal. These oxidation and reduction steps can be carried out in rapid succession or reduction can be carried out after a number of layers of oxide have been grown. This improved ALD approach achieves a greater degree of control over the formation of precursor monolayers since the precursor can strongly chemisorb onto an oxide or hydroxide type of surface rather than weakly absorbing onto a metallic surface. The precursors described in this disclosure are especially suited to this approach since they are hydrolytically labile. Thus, in the case of the binuclear complex, [-CuNMe₂SiMe₂CH₂CuNMe₂SiMe₂CH₂-], water vapor can break the Cu-CH₂ bond in the precursor by protonation of the carbon atom and break the Si-N bond by hydrolysis thereby yielding smaller molecular fragments that are more readily evacuated from the ALD chamber as volatile by products, as shown below in equation (f). This is illustrated by the result that in tetrahydrofuran solvent the [-CuNMe₂SiMe₂CH₂CuNMe₂SiMe₂CH₂-] complex is observed to release dimethylamine and hexamethyldisiloxane upon reaction with water.



The copper oxide thus produced is then reduced to copper metal by treatment with hydrogen gas, hydrogen plasma or other suitable reducing agent.

[0015] In summary, the process sequence for growing ALD copper using this superior process is as follows: a fresh metal, metal containing, metalloid, such as silicon or germanium, or metalloid containing surface is reacted with water, hydrogen peroxide, alcohol oxygen or other suitable reagent to give a new surface bearing hydroxyl OH, OH and oxide, or oxide oxygen groups. A monolayer of copper complex is then chemisorbed onto this surface to give copper oxide or hydroxide type species. A pulse of copper complex is then added to chemisorb a monolayer of it onto the hydroxide/oxide surface. The cycle of oxidant/copper precursor is continued until the desired thickness of oxide is achieved at which point the process is terminated by chemical reduction of the oxide layers to copper metal using a suitable volatile reducing agent, such as hydrogen, hydrogen plasma, silanes, and boranes. The thickness of the oxide layers is carefully chosen such that the oxide can be rapidly and completely reduced to metal. Once this is complete then the entire cycle can be restarted to yield an overall thicker final copper film. If the [-CuNMe₂SiMe₂CH₂CuNMe₂SiMe₂CH₂-] type precursor is utilized, it is thought that chemisorption onto a [-Cu-OH] surface site to form [Cu-O-Cu] should be strongly driven due to the basicity of the ligands driving proton removal from the OH group. This chemisorption is far stronger than the chemisorption of the same copper precursor directly onto a growing copper surface to give [-Cu-CuL-] type species which is representative of a typical ALD copper process. Thus greater control over monolayer saturation is achieved which is the key to a successful ALD approach. The resulting [-Cu-O-Cu] or [-Cu-O-Cu] surface is then reduced to [-Cu-Cu] to give a smooth copper film. This technique can also be applied to the formation of mixed metal alloy thin films by ALD. In this technique layers of copper oxide grown by ALD are alternated with additional layers of another metal oxide which can also be reduced to elemental metal by hydrogen or another reducing agent simultaneously with the reduction of copper oxide to copper metal. The ratio of copper oxide layers to alloying metal oxide layers determines the composition of the final metal alloy after reduction. For instance, copper oxide could be grown alternately with palladium oxide and this composite reduced to give a copper palladium alloy. Similarly, more than one additional metal oxide species can be incorporated into the copper oxide to yield, after reduction an alloy comprised of copper and at least two other metals. Specific copper alloys are more electromigration resistant than pure copper and hence are very important for the fabrication of copper interconnects. If the ALD copper alloy film forms a seed layer for subsequent electroplated copper, the alloying element(s) can be diffused into the bulk of the electroplated copper by applying a thermal anneal step resulting in a copper film containing uniformly distributed alloying elements.

[0016] Some copper alloys are advantageous for other reasons such as the alloying element segregating to the surface of the copper film after a thermal anneal whereupon it can be reacted with a processing gas or vapor to provide a protective layer. An example would be the growth and annealing of a copper/magnesium alloy whereby the magnesium segregates to the copper surface where it is subsequently oxidized to form a protective layer of magnesium oxide (Murarka, S., *Critical Reviews in Solid State and Materials Sciences*, 20 (2), pages 87-124 (1995)).

[0017] Other metals (M) can also be used instead of copper to give $[-\text{MNMe}_2\text{SiMe}_2\text{CH}_2\text{MNMe}_2\text{SiMe}_2\text{CH}_2-]$ type of complexes described in this disclosure thereby yielding volatile metal complexes other than copper that are usefull for CVD or ALD films containing those respective metals. Examples of such metals include, but are not limited to, silver, gold, cobalt, ruthenium, rhodium, platinum, palladium, nickel, osmium and iridium, sodium, potassium and lithium. Such complexes can also be used in conjunction with, or in alternating sequences with $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ type copper complexes to give copper alloys after a thermal anneal. Other metals that are divalent such as, but not limited to, palladium, platinum, rhodium and ruthenium can also be used to yield useful volatile complexes by coordinating ligands of the type shown in structure [1]. Such complexes can also be used in a simultaneous CVD deposition or ALD deposition with suitable copper complexes to yield copper alloys or other copper containing films. These new approaches to ALD copper and copper alloys and other copper containing films can also be applied using known copper precursors such as those described in the 10 groups below:

1) $\text{Cu}^{+1}(\beta\text{-diketonate})(\text{L})_n$ type precursors where (n) is 1 or 2 or where (L) represents an olefin, a diene, a tetraene, an alkyne trialkylsilylalkenes, trialkylsilyldienes trialkylsilyltetraenes, trialkylsilylacetylenes, trialkoxysilylalkenes, trialkoxysilyldienes trialkoxysilylacetylenes, trialkoxysilyldienes, trialkyl phosphines, and trialkoxyphosphines, nitriles, isonitriles, isocyanates, carbon monoxide, and and ($\beta\text{-diketonate}$) is represented by (hfac), acetylacetonate (i.e., acac), 3-halosubstituted acac; 1,5-dihalo substituted acac, 1,1,1-trihalosubstituted acac, alkylacetoacetates (methylacetoacetate), alkyl-oxobutanoates, aryl acetoacetates. $\beta\text{-diketonate}$ can also be substituted by aryl or alkyl substituted, halogenated, partly halogenated or non-halogenated $\beta\text{-diimine}$ or $\beta\text{-ketoimine}$, malonaldehyde, 2-halo-malonaldehyde, malonaldehyde diimines, dialkyl malonates (e.g. dimethyl malonate), diaryl malonates, arylalkyl malonates, 1,3-bis(trialkylsilyl)-1,3-propanedionate and 1-trialkylsilyl-3-alkyl-1,3-propanedionate.

2) $\text{Cu}^{+1}(\text{alkoxide})_n$ type precursors where (n) is typically from 4-6 and (alkoxide) represents t-butoxy, methoxy, ethoxy, isopropoxy, unsaturated alkoxides (e.g. 2-methyl-3-butene-2-oxy, 2-methyl-3-butene-2-oxy), alkynyl (e.g. propargyl alkoxide), allyloxy, vinyloxy, allylphenoxy, alkylphenoxy or mixtures thereof. Additional alkoxides include amino, imino, cyano and halogen substituted alkoxides, trialkylsilanoate, trialkoxysilanoate, dialkylalkylaminosilanoate, dialkylalkyliminosilanoate.

3) $[\text{Cu}^{+1}(\text{amide})]_n$ type precursors where (n) is typically 4-6 and (amide) represents secondary amide anion. Substituents on the amide nitrogen include but are not limited to the following representative groups: alkyl, aryl, allyl, arylalkyl, silylalkyl, silylaryl, alkylether, halogenated and partially halogenated dialkylsilyl.

4) $[\text{Cu}^{+1}(\text{R})]_n$ type precursors where (n) is typically between 4-6 and (R) represents alkyl, halogenated or partially halogenated alkyl, trialkoxysilylalkyl, trialkylsilylalkyl, trialkoxysilylalkyl, allyl, vinyl, alkynyl, aryl, mono and multi-alkyl substituted aryls, halo substituted aryls, arylalkyls, halo substituted aralkyls, alkoxy substituted aryls, alkoxy substituted aralkyls, iminosubstituted aryls and iminosubstituted alkyls.

5) $\text{Cu}^{+2} \text{bis}(\text{alkoxide})$ type precursors including, but not limited to, alkoxides substituted with amine, imine, ether, vinyl, alkynyl, aryl, trialkylsilyl or halogen. The alkoxide can also be dialkylalkylaminosilanoate or dialkylalkyliminosilanoate.

6) $\text{Cu}^{+2} \text{bis}[\beta\text{-diketonate}]$ type precursors where $[\beta\text{-diketonate}]$ can be substituted with alkyl, halogenated alkyl, vinyl, alkynyl, aryl, trialkylsilyl, halogen or ether groups.

7) $\text{Cu}^{+2} \text{bis}(\beta\text{-ketoimides})$ where the $\beta\text{-ketoimine}$ is substituted with alkyl, halogenated alkyl, trialkylsilyl, trialkoxysilyl, trialkylsiloxy, aryl, halogenated aryl, ether or amine groups.

8) $\text{Cu}^{+2}(\beta\text{-diimides})$ where the $\beta\text{-diimine}$ is substituted with hydrogen, alkyl, halogenated alkyl, trialkylsilyl, trialkoxysilyl, trialkylsiloxy, aryl, halogenated aryl, amine and ether groups.

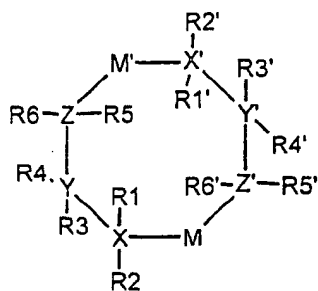
9) $\text{Cu}^{+1}(\text{amidinate})$ where (amidinate) represents alkyl-amidinate, aryl-amidinate, halo-amidinate, trialkylsilylamidinate, trialkylsilylalkylamidinate and trialkoxysilylamidinate structures.

10) $\text{Cu}^{+1}(\text{R})_n\text{L}$ type precursors where (n) is typically 1-3 and where (R) represents alkyl, halogenated alkyl, amine substituted alkyl, imine substituted alkyl allyl, vinyl, alkynyl, aryl, alkyl substituted aryls, halo substituted aryls, arylalkyls, halo substituted arylalkyls, alkoxy substituted aryls, alkoxy substituted arylalkyls, nitriles, haloalkanes, cyclopentadienyl, halogen substituted cyclopentadienyl, alkyl substituted cyclopentadienyl, halogenated alkyl substituted cyclopentadienyl. L is a neutral stabilizing ligand of the type trialkylphosphine, triarylphosphine, dialkyl-

phosphine, CO, nitrile, isonitrile, isocyanides, olefin, alkyne.

[0018] The ligand basicity of the $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ type complexes can also be used in another ALD approach where a monolayer of chemisorbed complex of the type [1] is treated with a volatile acid ligand such as a β -diketone which protonates off the ligand of the complex and in doing so forms a metastable copper (+1) (β -diketonate) species which then disproportionates to give volatile copper (+2) (β -diketonate)₂ and copper metal. This same chemistry can also be used in a CVD process for growing a copper film.

[0019] A structural representation of the metal complexes of this invention is shown below [1]



wherein M and M' are each a metal such as Cu, Ag, Au, and Ir; X and X' can be N or O; Y and Y' can be Si, C, Sn, Ge, or B; and Z and Z' can be C, N, or O. Substituents represented by R1, R2, R3, R4, R5, R6, R1', R2', R3', R4', R5', and R6' will vary depending on the ring atom to which they are attached. Additional embodiments include M and M' as divalent metals, such as Pt and Pd, where each metal center coordinates two of its own ligands.

[0020] A single crystal X-ray structure of one embodiment of the compounds of this invention, $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$, is shown in Fig. 1.

[0021] The eight membered cyclic core structure of this molecule constitutes a novel composition with unique metallization properties for copper and other metal CVD and ALD techniques, as mentioned above. Many variations of the above molecule are possible to bestow subtle changes in chemical and physical properties of the precursor. For instance, the periphery of the core structure can be modified by alkyl substitution to render the complex a liquid at room temperature

[0022] The following compositions are alternative preferred embodiments. In each of the following 12 types of compounds, M and M' are Cu. Different substitutions can be on X and X' (Group 1), Y and Y' (Group 2) and Z and Z' (Group 3). In all of the substitutions, alkyl and alkoxy can have 1 to 8 carbons, alkene, and alkyne can each have 2 to 8 carbons, and aryl can have 6 carbons.

[0023] The core ring structure, when X and X' are N, Y and Y' are Si, and Z and Z' are C, is $[-\text{Cu-N-Si-C-Cu-N-Si-C-}]$, denoted as Structure Type #1. Formulations for Structure Type #1:

Group 1: Substituents on X and X' (N)

[0024] R1, R2, R1', and R2' can be any combination of alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, or fluoroalkyl-substituted aryl.

Group 2: Substituents on Y and Y' (Si)

[0025] R3, R4, R3', and R4' can be any combination of alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, alkoxy, alkylamido, or halogen.

Group 3: Substituents on Z and Z' (C)

[0026] Either or all of R5, R6, R5' and R6' are hydrogen, alkenes, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, trialkylsilylalkyl, triarylsilyl, trialkylsiloxy, triarylsiloxy, trialkylsilanoate, alkoxy, trialkylsilylamido, or halogen.

[0027] Further, an analogous eight member ring core structure can also be created when Z and Z' are each N. This

would create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (N)(Group 1), Y and Y' (Si) (Group 2) and Z and Z' (N) (Group 3). The core ring structure is [-Cu-N-Si-N-Cu-N-Si-N-], denoted as Structure Type #2.

[0028] Formulations for Structure Type #2.

Group 1: Substituents on X and X' (N)

[0029] R1, R2, R1', and R2' can be any combination of hydrogen, alkyl, alkyne, alkene, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, or fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl.

Group 2: Substituents on Y and Y' (Si)

[0030] R3, R4, R3', and R4' can be any combination of alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, alkoxy, alkylamido, or halogen.

Group 3: Substituents on Z and Z' (N)

[0031] R5, R6, R5', and R6' are independently hydrogen, alkene, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, triarylsilyl, or halogen.

[0032] Further, an analogous eight member ring core structure can also be created when Z and Z' are each anionic O. This would create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for nitrogens X and X' (N)(Group 1), Y and Y' (Si) (Group 2). Different binuclear complexes are created by combining the following varyingly substituted Groups 1 and 2, along with Z and Z' (O), as they are connected together through two copper atoms to yield an eight membered ring. Thus, the core ring structure is [-Cu-N-Si-O-Cu-N-Si-O-], denoted as Structure Type #3.

[0033] Formulations for Structure Type #3.

Group 1: Substituents on X and X' (N)

[0034] R1, R2, R1', and R2' can be any combination of alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, or fluoroalkyl-substituted aryl.

Group 2: Substituents on Y and Y' (Si)

[0035] R3, R4, R3', and R4' can be any combination of alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, alkoxy, alkylamido, or halogen.

[0036] Further, an analogous eight member ring core structure can also be created Y and Y' are C. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for: X and X' (N)(Group 1), Y and Y' (C) (Group 2) and Z and Z' (C), (Group 3). Different binuclear complexes are created by combining the following varyingly substituted Groups 1, 2 and 3, as they are connected together through the two copper atoms to yield an eight membered ring. Thus, the core ring structure is [-Cu-N-C-C-Cu-N-C-C-], denoted as Structure Type #4.

[0037] Formulations for Structure Type #4.

Group 1: Substituents on X and X' (N)

[0038] R1, R2, R1', and R2' can be any combination of alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, or fluoroalkyl-substituted aryl.

Group 2: Substituents on Y and Y' (C)

[0039] R3, R4, R3', and R4' can be any combination of hydrogen, alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, alkoxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, or halogen.

Group 3: Substituents on Z and Z' (C)

[0040] Either or all of R5, R6, R5' and R6' are H, alkenes, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, trialkylsilylalkyl, triarylsilyl, trialkylsiloxy, triarylsi-

loxy, trialkylsilanoate, alkoxy, trialkylsilylamido, or halogen.

[0041] Further, an analogous eight member ring core structure can also be created when Y and Y' are C, and Z and Z' are N. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (N)(Group 1), Y and Y' (C) (Group 2) and Z and Z' (C) (Group 3). Different binuclear complexes are created by combining the following varyingly substituted Groups 1, 2 and 3. Thus, the core ring structure is [-Cu-N-C-N-Cu-N-C-N-], denoted as Structure Type #5.

[0042] Formulations for Structure Type #5.

Group 1: Substituents on X and X' (N)

[0043] R1, R2, R1', and R2' can be any combination of alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, or fluoroalkyl-substituted aryl.

Group 2: Substituents on Y and Y' (C)

[0044] R3, R4, R3', and R4' can be any combination of H, alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, alkoxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, or halogen.

Group 3: Substituents on Z and Z' (N)

[0045] R5, R6, R5', and R6' are independently hydrogen, alkene, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, triarylsilyl, or halogen.

[0046] Further, an analogous eight member ring core structure can also be created Y and Y' are C, and Z and Z' are O. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for nitrogens X and X' (N)(Group 1), Y and Y' (C) (Group 2). Different binuclear complexes are created by combining the following varyingly substituted Group 1, Group 2 and oxygens. Thus, the core ring structure is [-Cu-N-C-O-Cu-N-C-O-], denoted as Structure Type #6.

[0047] Formulations for Structure Type #6.

Group 1: Substituents on X and X' (N)

[0048] R1, R2, R1', and R2' can be any combination of alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, or fluoroalkyl-substituted aryl.

Group 2: Substituents on Y and Y' (C)

[0049] R3, R4, R3', and R4' can be any combination of H, alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, alkoxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, or halogen.

[0050] Further, an analogous eight membered ring core structure can also be created when X and X' are O. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (O) (Group 1), Y and Y' (Si) (Group 2) and Z and Z' (C) (Group 3). Different binuclear complexes are created by combining the following varyingly substituted Group 1, Group 2 and Group 3, as they are connected together through two copper atoms to yield an eight membered ring. Thus, the core ring structure is [-Cu-O-Si-C-Cu-O-Si-C-], denoted as Structure Type #7.

[0051] Formulations for Structure Type #7.

Group 1: Substituents on X and X' (O)

[0052] R1 and R1' are individually alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl. There is no substitution at R2 and R2'.

Group 2: Substituents on Y and Y' (Si)

[0053] R3, R4, R3', and R4' can be any combination of alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, alkoxy, alkylamido, or halogen.

Group 3: Substituents on Z and Z' (C)

[0054] Either or all of R5, R6, R5' and R6' are H, alkenes, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, trialkylsilylalkyl, triarylsilyl, trialkylsiloxy, triarylsiloxy, trialkylsilanoate, alkoxy, trialkylsilylamido, or halogen.

[0055] Further, an analogous eight membered ring core structure can also be created X and X' are O and Z and Z' are N. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (O) (Group 1), Y and Y' (Si) (Group 2) and Z and Z' (N) (Group 3). Thus, the core ring structure is $[-Cu-O-Si-N-Cu-O-Si-N-]$, denoted as Structure Type #8.

[0056] Formulations for Structure Type #8.

Group 1: Substituents on X and X' (O)

[0057] R1 and R1' are individually alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl. There is no substitution at R2 and R2'.

Group 2: Substituents on Y and Y' (Si)

[0058] R3, R4, R3', and R4' can be any combination of alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, alkoxy, alkylamido, or halogen.

Group 3: Substituents on Z and Z' (N)

[0059] R5, R6, R5', and R6' are independently hydrogen, alkene, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, triarylsilyl, or halogen.

[0060] Further, an analogous eight membered ring core structure can also be created when X and X' are O, and Z and Z' are O. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (O) (Group 1) and Y and Y' (Si) (Group 2). Thus, different binuclear complexes are created by combining the following varyingly substituted Group 1, Group 2 and oxygen atoms, as they are connected together through two copper atoms to yield an eight membered ring. Thus, the core ring structure is $[-Cu-O-Si-O-Cu-O-Si-O-]$, denoted as Structure Type #9.

[0061] Formulations for Structure Type #9.

Group 1: Substituents on X and X' (O)

[0062] R1 and R1' are individually alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl. There is no substitution at R2 and R2'.

Group 2: Substituents on Y and Y' (Si)

[0063] R3, R4, R3', and R4' can be any combination of alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, alkoxy, alkylamido, or halogen.

[0064] Further, an analogous eight membered ring core structure can also be created when X and X' is O and Y and Y' are C. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (O) (Group 1) and Y and Y' (C) (Group 2). Thus, different binuclear complexes are created by combining the following varyingly substituted Group 1, Group 2 and Group 3, as they are connected together through two copper atoms to yield an eight membered ring. Thus, the core ring structure is $[-Cu-O-C-C-Cu-O-C-C-]$, denoted as Structure Type #10.

[0065] Formulations for Structure Type #10.

Group 1: Substituents on X and X' (O)

[0066] R1 and R1' are individually alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl. There is no substitution at R2 and R2'.

Group 2: Substituents on Y and Y' (C)

[0067] R3, R4, R3', and R4' can be any combination of hydrogen, alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, alkoxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, or halogen.

Group 3: Substituents on Z and Z' (C)

[0068] Either or all of R5, R6, R5' and R6' are H, alkenes, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, trialkylsilylalkyl, triarylsilyl, trialkylsiloxy, triarylsiloxy, trialkylsilanoate, alkoxy, trialkylsilylamido, or halogen.

[0069] Further, an analogous eight membered ring core structure can also be created when X and X' are O, Y and Y' are C, and Z and Z' are N. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (O) (Group 1), Y and Y' (C) (Group 2) and Z and Z' (N). Thus, the core ring structure is [-Cu-O-C-N-Cu-O-C-N-], denoted as structure type #11.

[0070] Formulations for structure type #11.

Group 1: Substituents on X and X' (O)

[0071] R1 and R1' are individually alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl. There is no substitution at R2 and R2'.

Group 2: Substituents on Y and Y' (C)

[0072] R3, R4, R3', and R4' can be any combination of H, alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, alkoxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, or halogen.

Group 3: Substituents on Z and Z' (N)

[0073] R5, R6, R5', and R6' are independently hydrogen, alkene, alkyne, alkyl, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, triarylsilyl, or halogen.

[0074] Further, an analogous eight membered ring core structure can also be created when X and X' are O, Y and Y' are Si, and Z and Z' are O. This would also create another new class of CVD copper precursors, with great potential for yielding highly adherent films to tantalum. In the list below, different substitution groups are shown for X and X' (O) (Group 1), Y and Y' (C) (Group 2) and Z and Z' (O). Thus, the core ring structure is [-Cu-O-C-O-Cu-O-C-O-], denoted as Structure Type #12.

[0075] Formulations for Structure Type #12.

Group 1: Substituents on X and X' (O)

[0076] R1 and R1' are individually alkyl, alkynes, alkenes, partially fluorinated alkyl, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, trialkylsilyl, or triarylsilyl. There is no substitution at R2 and R2'.

Group 2: Substituents on Y and Y' (C)

[0077] R3, R4, R3', and R4' can be any combination of hydrogen, alkyl, partially fluorinated alkyl, trialkylsiloxy, triarylsiloxy, alkoxy, aryl, alkyl-substituted aryl, partially fluorinated aryl, fluoroalkyl-substituted aryl, or halogen.

[0078] A further series of structure types are also anticipated where the silicon atoms Y and Y' are substituted with either tin atoms, germanium atoms, boron atoms or aluminum atoms.

[0079] For tin, the core structures would become [-Cu-O-Sn-O-Cu-O-Sn-O-], [-Cu-O-Sn-N-Cu-O-Sn-N-] (two classes since O can be either an ether or anionic oxygen), [-Cu-N-Sn-N-Cu-N-Sn-N-], [-Cu-O-Sn-C-Cu-O-Sn-C-], or [-Cu-N-Sn-C-Cu-N-Sn-C-] listed below as Structure Types 19, 20, 21, 22, 23, 24, respectively. For germanium substituted for Y and Y', an analogous series of compounds are also generated.

[0080] Substitution on Z and Z', when they are oxygen, nitrogen or carbon, for both the tin and germanium-based structures, can be as listed for the substitution patterns on these elements as shown for Structure Types 1-12. Substitution on tin or germanium can be as listed for substitution on Si in Structure Types 1-12. By substituting tin for silicon in the compounds listed as synthetic precursors materials for Structure Types 1, 2, 3, 7, 8 and 9, then following the same synthetic steps for the latter compounds, synthetic routes to Structure Types 19, 20, 21, 22, 23 and 24, along

with the analogous germanium based series of Structure Types is achieved.

[0081] For boron, the Structure Types would thus become [-Cu-O-B-O-Cu-O-B-O-], [-Cu-O-B-N-Cu-O-B-N-] (two classes since O can be either an ether or anionic oxygen), [-Cu-N-B-N-Cu-N-B-N-], [Cu-O-B-C-Cu-O-B-C-], [-Cu-N-B-C-Cu-N-B-C-]. These are listed below as Structure Types 13, 14, 15, 16, 17 and 18, respectively. When Y and Y' are Al, an analogous series of Structure Types can be generated. Substituents on oxygen or nitrogen or carbon (Z and Z') for both the aluminum and boron based-Structure Types is to be as, but not limited to, those listed for oxygen, nitrogen and carbon in Structure Types 1-12. Boron or aluminum substituents can include, but not be limited to, halogen (especially fluorine), C₁-C₈ alkyl and fluoroalkyl, aryl and fluoroaryl, partially fluorinated or unfluorinated alkoxide or silanoate, amide.

CVD and ALD processes

[0082] It is anticipated that the CVD and ALD processes for growing pure copper metal, copper metal containing metallic alloys, and other copper containing films or other metal films using the above complexes will operate effectively under the following process conditions in any combination:

- (a) within a temperature range of zero to 500 degrees Celcius
- (b) within a pressure range of 1 mTorr to greater than 760 Torr
- (c) with the use of microwave generated plasma, either remote or direct
- (d) with the use of the following reagent gases added stoichiometrically or catalytically:
hydrogen, ammonia, water vapor, oxygen, nitrous oxide, hydrazines, amines, alcohols, phosphines, silanes, boranes, alanes, or other chemically reactive species capable of yielding metal containing films from these metal precursors.
- (e) vapors of other metal precursors in conjunction with reagent gases as in (d) to grow copper metal alloys or other mixed metal compounds, including copper. An example would be superconducting YBaCu oxides.
- (f) Volatile sulfur containing volatile compounds can be added during the CVD process to form metal sulfides.

[0083] Any of the above compounds may also form useful precursors for copper CVD when complexed to various neutral ligands, such as; alcohols ethers, amines, alkenes, alkynes, arenes, phosphines, carbon monoxide, nitriles, isonitriles, cyanates, or isocyanates, imines, diimines, nitrogen containing heterocycles.

[0084] Especially beneficial compositions may be those complexes that are liquid or especially volatile.

[0085] In the above complexes where the ligand system is not bearing oxygen, for instance the Cu-N-Si-C-Cu-N-Si-C system, it is anticipated that volatile complexes of oxophilic metals such as magnesium, zirconium, etc., could be prepared that would be chemically compatible with copper complexes prepared from the same or similar ligands. CVD using a mixture of two such compounds should permit the deposition of copper alloys, such as; Cu/Mg or Cu/Zr, which are known to possess properties of enhanced reliability and improved electromigration resistance. With the selection of appropriate ligands, such mixtures can be prepared that are liquid blends, and thus, especially suited to direct liquid injection delivery to the CVD chamber.

[0086] Further, selected substituents on selected atoms that form the core eight membered rings in all of the above compounds may also include groups containing tin, such that this element can become intermingled with the copper CVD film to give an alloy that is more electromigration resistant than pure copper.

EXPERIMENTAL

SYNTHESIS

[0087] The [-CuNMe₂SiMe₂CH₂CuNMe₂SiMe₂CH₂-] complex was synthesized as follows. Under a blanket of nitrogen, 15.1g (0.1 moles) of dimethylaminochloromethyldimethylsilane was added to 2.4g (0.1 moles) of magnesium in 200 ml dry tetrahydrofuran. The mixture was stirred overnight at room temperature to give a gray solution. 8.5 ml of dioxane was added in one lot, stirred for 30 mins. and then the resulting magnesium chloride/dioxane precipitate was filtered off. The filtrate was then cooled on an ice bath to 6 degrees centigrade and 10g of cuprous chloride (0.1 moles) was added over 1 hour with stirring. The mix was stirred one further hour at 6 degrees centigrade and then allowed to warm to room temperature with continued stirring. This mixture was filtered, and the filtrate stripped of solvent at room temperature to give an off-white solid. This solid was placed in a sublimator at 105 degrees centigrade and sublimed under dynamic vacuum at 0.001 Torr to give a colorless crystalline sublimate of the complex [-CuNMe₂SiMe₂CH₂CuNMe₂SiMe₂CH₂-] Yield = 5.0 g

¹HNMR in deuterobenzene: singlet at 2.22 ppm (6H), singlet at 0.21 ppm (6H), singlet at -0.33 ppm (2H).

¹³C NMR in deuterobenzene: singlet at -8.2 ppm, singlet at -0.25 ppm, singlet at 40.1 ppm.

GCMS analysis of the purified $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ complex showed predominantly the product of ligand coupling, i.e., $\text{Me}_2\text{NSiMe}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiNMe}_2$, due to thermal reaction in the GC injector port.

[0088] In other experiments it was found that the application of excessive heat greater than 120°C during sublimation of the $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ complex also begins to yield a copper film and the coupled ligand $\text{Me}_2\text{NSiMe}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiNMe}_2$ as the sole volatile by product, identified by both GCMS and $^1\text{HNMR}$. As shown below, under CVD conditions we also observed the coupling of the ligands in the $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ complex simultaneous with growing a copper containing film.

CVD

[0089] Using a Vactronics LPCVD reactor the following conditions were used:

Precursor	$[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$
Substrate	Tantalum sputtered onto a silicon wafer
Precursor delivery temperature	75°C
Chamber pressure	1.5 Torr
Wafer temperature	143°C
Carrier gas flow rate	70 sccm
Diluent gas flow rate	100 sccm

[0090] This provided a copper containing film, as determined by an EDX scan.

Mass spectral analysis of the CVD chamber gases during processing revealed the presence of $\text{NMe}_2\text{SiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{NMe}_2$ as a peak at 188 mu (parent ion of 232 mu minus $(\text{Me})_2\text{N}$ of 44 mu) from the coupling of the ligand system in the precursor $[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$ as it releases copper metal in the CVD process.

[0091] The essence of the above synthesis is metallation of a methyl group alpha to silicon in dimethylaminotrimethylsilane followed by reaction with a copper (+1) species

[0092] The resulting reaction mixture is then filtered, if necessary, to remove any by-product precipitates and then sublimed to yield the final product. In some instances it may be possible to sublime the final product directly from the crude reaction mixture.

[0093] Metallation of the dimethylaminotrimethylsilane can be accomplished in many ways and a wide range of copper (+1) reagents can be selected for reaction with it in the course of pursuing alternative synthetic routes to complexes of the type [1] as shown above. For example, in the case of preparing

$[-\text{CuNMe}_2\text{SiMe}_2\text{CH}_2\text{CuNMe}_2\text{SiMe}_2\text{CH}_2-]$, dimethylaminotrimethylsilane can be effectively metallated by first forming a dimethylaminohalomethyltrimethylsilane and reacting it with a metal such as, but not limited to, magnesium, lithium, aluminum, sodium, potassium, cesium, rubidium. Alternatively, the dimethylaminohalomethyltrimethylsilane can be reacted with an organometallic species to undergo a metal/halogen to generate the metallated dimethylaminotrimethylsilane species. Alternatively, dimethylaminotrimethylsilane can be deprotonated using an organometallic reagent. Alternatively, the metallated dimethylaminotrimethylsilane species can be generated electrochemically. Suitable copper (+1) sources for which to react the thus metallated dimethylaminotrimethylsilane include, but are not limited to, copper halides, copper acetate, copper trifluoroacetate, copper triflate, copper alkoxides, copper amides, copper organometallics, copper hexafluorophosphate, copper tetrafluoroborate or other suitable copper(+1) compounds. The final product may be purified by sublimation, distillation, recrystallization, selective reversible absorption, selective and reversible adduct formation with a suitable coordinating medium, column chromatography using a chromatographic medium that is benign towards the organometallic copper compound product.

[0094] The general principles of the above alternative syntheses can also be expanded to include dialkylaminotrimethylsilane species in general in addition to the syntheses listed below, and metals other than copper can be used to prepare the final metal complex.

[0095] Other Structure Type #1 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #2 compounds

[0096] Dimethyldichlorosilane (1 mole) can be dissolved in one liter of tetrahydrofuran under an atmosphere of nitrogen, to which one mole of lithiummethylamide in one liter of tetrahydrofuran can be slowly added. The resulting mixture can be stirred overnight, then all volatiles can be vacuum transferred off and fractionally distilled under an atmospheric pressure of nitrogen to give methylaminodimethylchlorosilane. One half mole of methylaminodimethylchlorosilane can be then dissolved in one liter of tetrahydrofuran under an atmosphere of nitrogen, to which lithium-

dimethylamide as a suspension in hexane can be slowly added. The resulting solution can be stirred overnight at room temperature, all volatiles can be vacuum transferred off, and the resulting mixture can be fractionally distilled to give the product dimethylaminomethylaminodimethylsilane.

[0097] One tenth of a mole of dimethylaminomethylaminodimethylsilane can be then suspended in 100 ml tetrahydrofuran under a blanket of nitrogen, and one tenth of a mole of normal-butyl lithium (nBuLi) in hexane can be added over 10 minutes. The resulting solution can be cooled to zero degrees centigrade, and one tenth of a mole of copper chloride can be added over 1 hour. The resulting mixture would be allowed to warm to room temperature for 1 hour, then filtered. The filtrate can be stripped of solvent and heated under vacuum to distill out the product [-Cu-NMe₂SiMe₂NMe-Cu-NMe₂SiMe₂NMe-].

Synthesis of a compound of Structure Type #3 compounds

[0098] One mole of diethyldichlorosilane can be dissolved in one liter of tetrahydrofuran, or similar solvent, under an atmosphere of nitrogen, and one mole of lithium dimethylamide can be slowly added with stirring over a one hour period, then stirred overnight. All of the volatiles can be vacuum transferred off and fractionally distilled to yield the product, dimethylaminodiethylchlorosilane. This product can be dissolved in tetrahydrofuran, or similar solvent, under a nitrogen atmosphere. One mole of water can be dissolved in 100 ml of tetrahydrofuran, or similar solvent, and can be added slowly over a one hour period at zero degrees centigrade. The resulting mixture can be filtered, and the filtrate fractionally distilled to give the product, dimethylaminodiethylsilanol. One equivalent of this product can be dissolved in tetrahydrofuran, or in a similar solvent, and treated with one equivalent of n-butyl lithium solution. The mixture can be cooled to zero degrees centigrade, and one equivalent of copper chloride can be added over 30 minutes. The mixture would be allowed to warm to room temperature, filtered, solvent stripped away, and the resulting mixture can be heated under vacuum to distill out the product, [Cu-NMe₂-SiEt₂-O-Cu-NMe₂-SiEt₂-O-Cu-].

Synthesis of a compound of Structure Type #4.

[0099] Dimethylamino-iodomethylmethane can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be then dissolved in tetrahydrofuran, or a similar solvent, and can be reacted with one equivalent of magnesium and allowed to stir overnight. One equivalent of dioxane can be added and after 30 minutes the mixture can be filtered. This solution can be cooled to zero degrees celsius and cuprous chloride, or other suitable cuprous compound can be slowly added over one hour. This mixture can be allowed to stir at room temperature for one hour. The solvent can be vacuum stripped off, and the resulting solid can be heated under vacuum to distill out the product as [-Cu-NMe₂-CH₂-CH₂-Cu-NMe₂-CH₂-CH₂-]. Other Structure Type #4 compounds may also be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #5 .

[0100] N-dimethylamino-N'-methylaminodimethylmethane can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, cooled to -78°C and one equivalent of nBuLi can be added. The mixture can be allowed to warm to room temperature and stirred overnight. To this mixture one equivalent of cuprous chloride or similar cuprous reagent can be slowly added over one hour, and the mixture can be allowed to stir at room temperature for one hour. The solvent can be vacuum stripped off, and the resulting solid can be heated under vacuum to distill out the product as [-Cu-NMe₂-CMe₂-NMe-Cu-NMe₂-CMe₂-NMe-]. Other Structure Type #4 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #6 .

[0101] Dimethylaminomethanol can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, cooled to zero degrees celsius and can be reacted with one equivalent of sodium hydride or similar deprotonating agent. This mixture can be allowed to warm to room temperature and stirred overnight. To this mixture one equivalent of cuprous chloride or similar cuprous reagent can be slowly added over one hour, and the mixture allowed to stir at room temperature for one hour. The solvent can be vacuum stripped off and the resulting solid can be heated under vacuum to distill out the product as [-Cu-NMe₂-CH₂-O-Cu-NMe₂-CH₂-O-]. Other Structure Type #6 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #7

[0102] t-Butoxychloromethyldimethylsilane can be synthesized using standard organic synthetic techniques. One

equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, and can be reacted with one equivalent of magnesium and can be allowed to stir overnight. One equivalent of dioxane can be added, and after 30 minutes, the mixture can be filtered. This solution can be cooled to zero degrees celsius, and cuprous chloride, or other suitable cuprous compound can be slowly added over one hour. This mixture can be allowed to stir at room temperature for one hour. The mixture can be filtered, and the solvent can be vacuum stripped off from the filtrate. The resulting solid can be heated under vacuum to distill out the product as $[-\text{Cu}-(\text{CH}_3)_3\text{O}-\text{CH}_2-\text{CH}_2-\text{Cu}-(\text{CH}_3)_3\text{O}-\text{CH}_2-\text{CH}_2-]$. Other Structure Type #7 compounds may also be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #8

[0103] Methoxymethylaminodimethylsilane can be synthesised using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, cooled to zero degrees celsius and can be reacted with one equivalent of n-butyllithium or similar deprotonating agent. This mixture can be allowed to warm to room temperature and can be stirred overnight. To this mixture one equivalent of cuprous chloride or similar cuprous reagent can be slowly added over one hour, and the mixture can be allowed to stir at room temperature for one hour. The mixture can be filtered, solvent can be vacuum stripped from the filtrate and the resulting solid can be heated under vacuum to distill out the product as $[-\text{Cu}-\text{OMe}-\text{SiMe}_2-\text{NMe}-\text{Cu}-\text{OMe}-\text{SiMe}_2-\text{NMe}-]$. Other Structure Type #8 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #9

[0104] Methoxydimethylsilanol can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, cooled to zero degrees celsius and can be reacted with one equivalent of sodium hydride or similar deprotonating agent. This mixture can be allowed to warm to room temperature and can be stirred overnight. To this mixture one equivalent of cuprous chloride or similar cuprous reagent can be slowly added over one hour, and the mixture can be allowed to stir at room temperature for one hour. The mixture can be filtered, solvent can be vacuum stripped from the filtrate and the resulting solid can be heated under vacuum to distill out the product as $[-\text{Cu}-\text{OMe}-\text{SiMe}_2-\text{O}-\text{Cu}-\text{OMe}-\text{SiMe}_2-\text{O}-]$. Other Structure Type #9 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #10

[0105] t-Butoxy-bromomethylmethane can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, and can be reacted with one equivalent of magnesium and allowed to stir overnight. One equivalent of dioxane can be added, and after 30 minutes, the mixture is filtered. This solution can be cooled to zero degrees celsius and cuprous chloride, or other suitable cuprous compound can be slowly added over one hour. This mixture can be allowed to stir at room temperature for one hour. The mixture can be filtered, and the solvent can be vacuum stripped off from the filtrate. The resulting solid can be heated under vacuum to distill out the product as $[-\text{Cu}-\text{Ot}-\text{Bu}-\text{CH}_2-\text{CH}_2-\text{Cu}-\text{Ot}-\text{Bu}-\text{CH}_2-\text{CH}_2-]$. Other Structure Type #10 compounds may also be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #11

[0106] Methoxymethylaminomethane can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, cooled to zero degrees celsius and can be reacted with one equivalent of n-butyllithium or similar deprotonating agent. This mixture can be allowed to warm to room temperature and can be stirred overnight. To this mixture one equivalent of cuprous chloride or similar cuprous reagent can be slowly added over one hour, and the mixture can be allowed to stir at room temperature for one hour. The mixture can be filtered, solvent can be vacuum stripped from the filtrate, and the resulting solid can be heated under vacuum to distill out the product as $[-\text{Cu}-\text{OMe}-\text{CH}_2-\text{NMe}-\text{Cu}-\text{OMe}-\text{CH}_2-\text{NMe}-]$. Other Structure Type #11 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #12

[0107] t-Butoxymethanol can be synthesized using standard organic synthetic techniques. One equivalent of this compound can be dissolved in tetrahydrofuran, or a similar solvent, cooled to zero degrees celsius and can be reacted with one equivalent of sodium hydride or similar deprotonating agent. This mixture can be allowed to warm to room temperature and can be stirred overnight. To this mixture one equivalent of cuprous chloride or similar cuprous reagent

can be slowly added over one hour, and the mixture can be allowed to stir at room temperature for one hour. The mixture can be filtered, solvent can be vacuum stripped from the filtrate and the resulting solid can be heated under vacuum to distill out the product as [-Cu-Ot-Bu-CH₂-O-Cu-Ot-Bu-CH₂-O-] Other Structure Type #12 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #13

[0108] Using standard boron chemistry synthetic techniques, MeOB(Me)OH can be prepared. This compound can be dissolved in ether or another suitable solvent under an atmosphere of nitrogen and can be treated with one equivalent of sodium hydride or other suitable deprotonating agent. This mixture can be treated with one equivalent of copper chloride or other suitable cuprous source. After a suitable reaction time, this mixture can be filtered, the filtrate can be stripped of solvent, and the resulting material can be heated under vacuum to distill out the product [-Cu-OMe-BMe-O-]. Other Structure Type #13 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #14

[0109] Using standard boron chemistry synthetic techniques, MeOB(Me)NMeH can be prepared. This compound can be dissolved in ether or another suitable solvent under an atmosphere of nitrogen and can be treated with one equivalent of sodium hydride or other suitable deprotonating agent. This mixture can be treated with one equivalent of copper chloride or other suitable cuprous source. After a suitable reaction time, this mixture can be filtered, the filtrate can be stripped of solvent and the resulting material can be heated under vacuum to distill out the product [-Cu-OMe-BMe-NMe-Cu-OMe-BMe-NMe-]. Other Structure Type #14 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #15

[0110] Using standard Boron chemistry synthetic techniques, HOB(Me)NMe₂ can be prepared. This compound can be dissolved in ether or another suitable solvent under an atmosphere of nitrogen and can be treated with one equivalent of sodium hydride or other suitable deprotonating agent. This mixture can be treated with one equivalent of copper chloride or other suitable cuprous source. After a suitable reaction time this mixture can be filtered, the filtrate can be stripped of solvent and the resulting material heated under vacuum to distill out the product [-Cu-O-BMe-NMe₂-Cu-O-BMe-NMe₂-]. Other Structure Type #15 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #16

[0111] Using standard Boron chemistry synthetic techniques, HMeNB(Me)NMe₂ can be prepared. This compound can be dissolved in ether or another suitable solvent under an atmosphere of nitrogen and can be treated with one equivalent of sodium hydride or other suitable deprotonating agent. This mixture can be treated with one equivalent of copper chloride or other suitable cuprous source. After a suitable reaction time, this mixture can be filtered, the filtrate can be stripped of solvent and the resulting material can be heated under vacuum to distill out the product [-Cu-NMe-BMe-NMe₂-Cu-NMe-BMe-NMe₂-]. Other Structure Type #16 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #17

[0112] Using standard Boron chemistry synthetic techniques, MeO-B(Me)CH₂Br can be prepared. This compound can be dissolved in ether or another suitable solvent under an atmosphere of nitrogen and can be treated with one equivalent of magnesium. This mixture can be allowed to stir overnight, then can be treated with one equivalent of dioxane and can be filtered. To this filtrate, one equivalent of copper chloride or other suitable cuprous source can be added. After a suitable reaction time, this mixture can be filtered, the filtrate can be stripped of solvent and the resulting material can be heated under vacuum to distill out the product [-Cu-OMe-BMe-CH₂-Cu-OMe-BMe-CH₂-]. Other Structure Type #17 compounds may be prepared using analogous syntheses.

Synthesis of a compound of Structure Type #18

[0113] Using standard Boron chemistry synthetic techniques, Me₂N-B(Me)CH₂Br can be prepared. This compound can be dissolved in ether or another suitable solvent under an atmosphere of nitrogen and can be treated with one equivalent of magnesium. This mixture can be allowed to stir overnight, then can be treated with one equivalent of

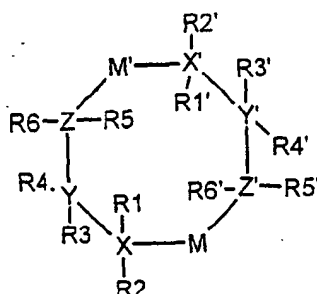
dioxane and can be filtered. To this filtrate, one equivalent of copper chloride or other suitable cuprous source can be added. After a suitable reaction time, this mixture can be filtered, the filtrate can be stripped of solvent and the resulting material can be heated under vacuum to distill out the product $[-\text{Cu-NMe}_2\text{-BMe-CH}_2\text{-Cu-NMe}_2\text{-BMe-CH}_2\text{-}]$. Other structure type #18 compounds may be prepared using analogous syntheses.

[0114] Within each of the structure types shown above there are the groups 1, 2 and 3 that can bear different substituents. In a typical synthesis, a complex is designed by selecting which substituted groups 1, 2 and 3 will comprise the ligand and after it is synthesized and complexed to copper or another metal, a discrete compound is formed. However, it may be advantageous to select two or more different patterns of substitution within the groups to yield two or more different ligands as, as a mixture these ligands are complexed to copper or other metal to create a mixture of copper or other metal compounds. Since there are two ligands and two copper centers per molecule of final product, if ligands L1 and L2 constitute the mixture of ligands which is complexed to copper, then a mixture of three copper complexes will form, i.e., $\text{Cu}_2(\text{L1})_2$, $\text{Cu}_2(\text{L1})(\text{L2})$, and $\text{Cu}_2(\text{L2})(\text{L2})$. Similarly, a mixture of three different ligands will yield a mixture of copper complexes described as $\text{Cu}_2(\text{L1})_2$, $\text{Cu}_2(\text{L2})_2$, $\text{Cu}_2(\text{L3})_2$, $\text{Cu}_2(\text{L1})(\text{L2})$, $\text{Cu}_2(\text{L2})(\text{L3})$ and $\text{Cu}_2(\text{L1})(\text{L3})$. The advantage of such mixtures is that they can be manifest as liquids which, under certain circumstances, may offer advantages in vapor delivery, especially by the process of direct liquid injection in the CVD or ALD process.

[0115] The present invention has been set forth with regard to several preferred embodiments, but the full scope of the present invention should be ascertained from the claims which follow.

Claims

1. A compound represented by the structure:



wherein

M and M' are each a metal;

X and X' are each N or O;

Y and Y' are each Si, C, Sn, Ge, B, or Al;

Z and Z' are each C, N, or O;

R1, R2, R1', and R2' are each independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, or a triarylsilyl;

R3, R4, R3', and R4' are each independently H, an alkyl, a partially fluorinated alkyl, a trialkyl siloxy, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, an alkoxy, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, a triarylsilyl, a bis(trialkylsilyl)amido, a bis(triarylsilyl)amido, or a halogen; and

R5, R6, R5', and R6' are each independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, a halogen, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, a triarylsilyl, a trialkylsilanoate, or an alkoxy;

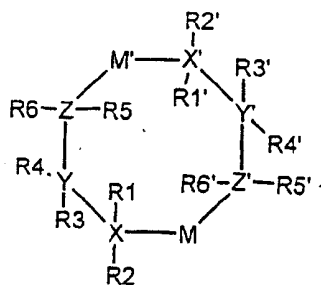
provided that when X and X' are each O, there is no substitution at R2 and R2';

further provided that when Z and Z' are each O, there is no substitution at R5, R6, R5', or R6';

said alkyl and alkoxy having 1 to 8 carbons; said alkenyl and alkynyl having 2 to 8 carbons; and said aryl having 6 carbons.

2. The compound of claim 1 wherein M and M' are each Cu.

3. The compound of claim 1 wherein X and X' are each N.
4. The compound of claim 3 wherein Y and Y' are each Si.
5. The compound of claim 4 wherein Z and Z' are each C.
6. A compound represented by the structure:



wherein

M and M' are each Cu;

X and X' are each N;

Y and Y' are each Si;

Z and Z' are each C;

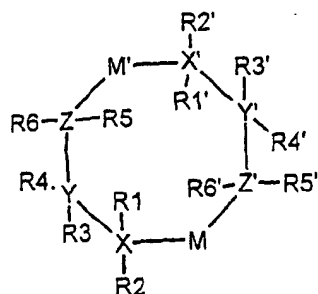
R1, R2, R1', and R2' are each independently an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, or a fluoralkyl-substituted aryl;

R3, R4, R3', and R4' are each independently a C₁-C₈ alkyl, a partially fluorinated alkyl, a trialkyl siloxy, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, an alkoxy, or a halogen; and each of R5, R6, R5', and R6' are independently H, an alkyl, an alkene, an alkyne, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoralkyl-substituted aryl, a halogen, a trialkylsilyl, a triarylsilyl, a trialkylsilanoate, or an alkoxy;

said alkyl and alkoxide having 1 to 8 carbons; said alkenyl and alkynyl having 2 to 8 carbons; and said aryl having 6 carbons.

7. The compound of claim 6 wherein R1, R2, R3, R4, R1', R2', R3', and R4' are each methyl; and R5, R6, R5', and R6' are each H.
8. The compound of claim 6 wherein R1, R2, R3, R4, R1', R2', R3', and R4' are each methyl; R5 and R5' are each trimethylsilyl; and R6 and R6' are each H.
9. A method of forming a metal or metal-containing film on a substrate, under ALD conditions, comprising

- (a) reacting a metal substrate, a metal containing substrate, a metalloid substrate, or a metalloid-containing substrate surface with an appropriate reagent to give a surface bearing hydroxyl OH or oxide oxygen;
- (b) chemisorbing a layer of a composition comprising a metal complex of structure [1] onto the surface bearing hydroxyl OH or oxide oxygen to form a newly metal functionalized surface;



[1]

wherein M and M' are each a metal;

X and X' are each N or O;

Y and Y' are each Si, C, Sn, Ge, B, or Al;

Z and Z' are each C, N, or O;

R1, R2, R1', and R2' are each independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl or a triarylsilyl;

R3, R4, R3', and R4' are each independently H, an alkyl, a partially fluorinated alkyl, a trialkyl siloxy, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, an alkoxy, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, a triarylsilyl, a bis(trialkylsilyl)amido, a bis(triarylsilyl)amido, or a halogen; and

R5, R6, R5', and R6' are each independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, a halogen, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, a triarylsilyl, a trialkylsilanoate, or an alkoxy;

provided that when X and X' are each O, there is no substitution at R2 and R2';

further provided that when Z and Z' are each O, there is no substitution at R5, R6, R5', or R6';

said alkyl and alkoxy having 1 to 8 carbons; said alkenyl and alkynyl having 2 to 8 carbons; and said aryl having 6 carbons;

(c) oxidizing or hydroxylating the newly metal functionalized surface to form a metal oxide layer;

(d) repeating the above steps (b) and (c) as needed to build a required number of metal oxide layers for a thickness which can be chemically reduced; and

(e) reducing the metal oxide layers to form a smooth metal film; and

(f) optionally repeating steps (a) through (e) to grow a thicker metal film.

10. The method of claim 9 wherein said substrate is silicon or germanium.

11. The method of claim 10 wherein M and M' are selected from the group consisting of Cu, Ag, Au, and Ir.

12. The method of claim 10 wherein M and M' are each Cu.

13. The method of claim 12 wherein X and X' are each N.

14. The method of claim 13 wherein Y and Y' are each Si.

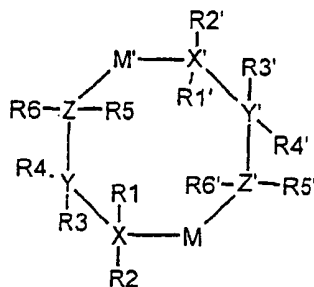
15. The method of claim 14 wherein Z and Z' are each C.

16. The method of claim 10 wherein M and M' are different metals in each layer when there is more than one layer.

17. The method of claim 10 wherein the composition of (b) also comprises another metal precursor selected from the groups consisting of a metal β -diketonate; a metal alkoxide; a metal amide; a metal bis(alkoxide); a metal bis (β -ketonate); a metal bis (β -ketoimide); a metal (β -diimide); and a metal (amidinate).

18. A method of forming a metal or metal-containing film comprising reacting, under chemical vapor deposition con-

ditions sufficient to deposit a film on a substrate, a precursor represented by the structure:



wherein

M and M' are each a metal;

X and X' are each N or O;

Y and Y' are each Si, C, Sn, Ge, B, or Al;

Z and Z' are each C, N, or O;

R1, R2, R1', and R2' are each independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl; a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, or a triarylsilyl;

R3, R4, R3', and R4' are each independently H, an alkyl, a partially fluorinated alkyl, a trialkyl siloxy, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, an alkoxy, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, a triarylsilyl, a bis(trialkylsilyl)amido, a bis(triarylsilyl)amido, or a halogen; and

R5, R6, R5', and R6' are each independently H, an alkyl, an alkenyl, an alkynyl, a partially fluorinated alkyl, an aryl, an alkyl-substituted aryl, a partially fluorinated aryl, a fluoroalkyl-substituted aryl, a halogen, a trialkylsiloxy, a triarylsiloxy, a trialkylsilyl, a triarylsilyl, a trialkylsilanoate, or an alkoxy;

provided that when X and X' are each O, there is no substitution at R2 and R2';

further provided that when Z and Z' are each O, there is no substitution at R5, R6, R5', or R6';

said alkyl and alkoxide having 1 to 8 carbons; said alkenyl and alkynyl having 2 to 8 carbons; and said aryl having 6 carbons.

19. The method of claim 18 wherein M and M' are selected from the group consisting of selected from the group consisting of Cu, Ag, Au, Os, and Ir.

20. The method of claim 18 wherein M and M' are each Cu.

21. The method of claim 20 wherein X and X' are each N.

22. The method of claim 21 wherein Y and Y' are each Si.

23. The method of claim 22 wherein Z and Z' are each C.

24. The method of claim 18 wherein M and M' are each Pt, Pd, Rh, or Ru.

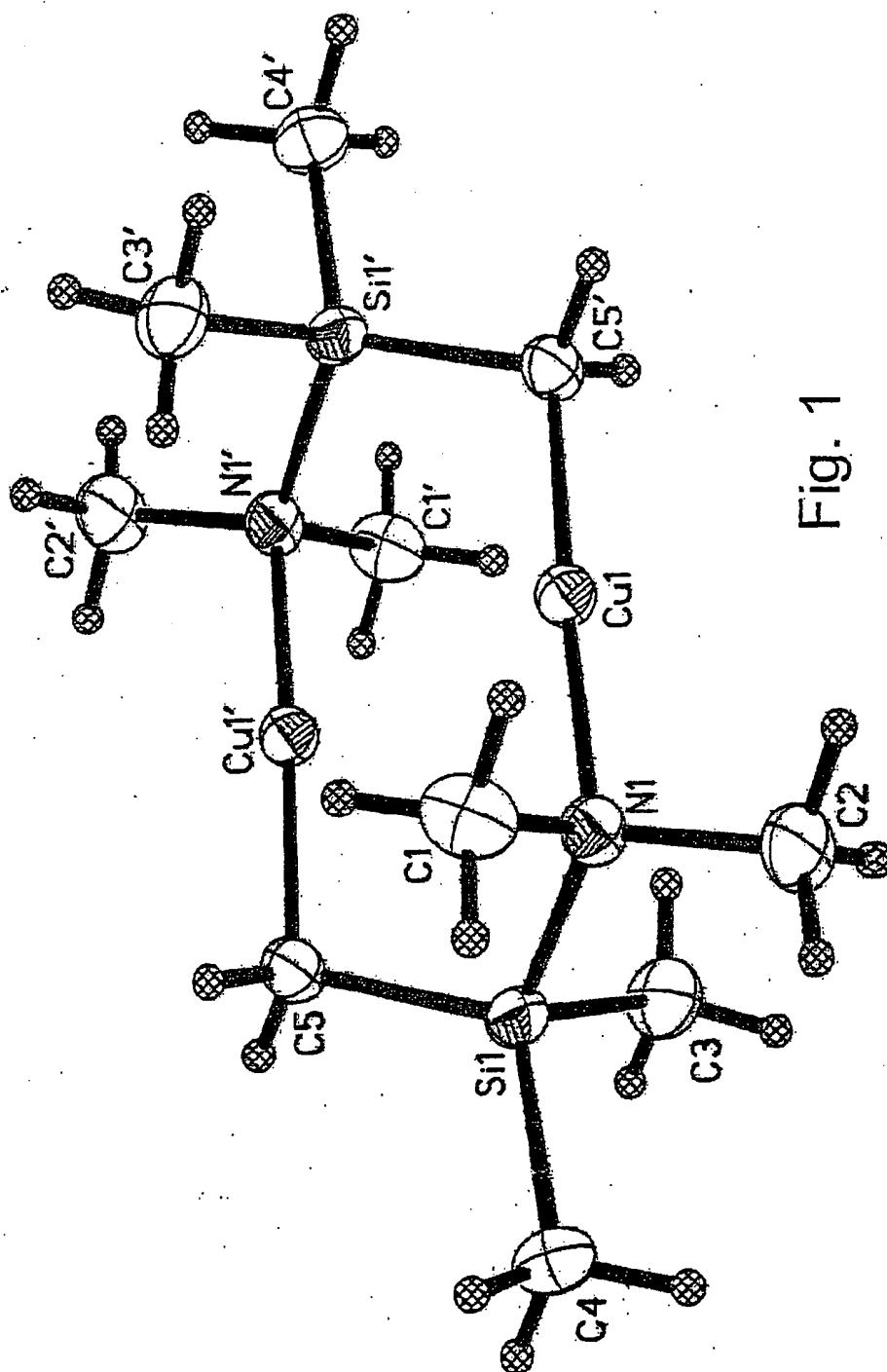


Fig. 1

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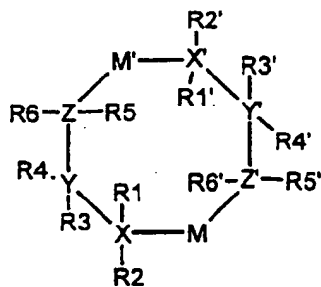
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(54) Volatile precursors for deposition of metals and metal-containing films

(57) This invention is directed to a group of novel homologous eight membered ring compounds having a metal, such as copper, reversibly bound in the ring and containing carbon, nitrogen, silicon and/or other metals. A structural representation of the compounds of this invention is shown below:



wherein M and M' are each a metal such as Cu, Ag, Au and Ir; X and X' can be N or O; Y and Y' can be Si, C; Sn, Ge, or B; and Z and Z' can be C, N, or O. Substituents represented by R1, R2, R3, R4, R5, R6, R1', R2', R3', R4', R5', and R6' will vary depending on the ring atom to which they are attached. This invention is also directed to depositing metal and metal-containing films on a substrate, under ALD or CVD conditions, using the above novel compounds as precursors.

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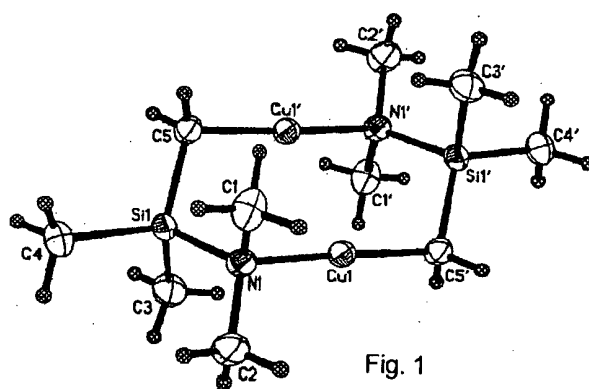


Fig. 1



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; BECKMANN, JENS ET AL: "The first organoelement oxides containing three different metals; synthesis and structure of (Ph₂SiOR₂SnOMO) [R = (CH₂)₃NMe₂; M = But₂Sn, But₂Ge, PhB].dag..dbldag." retrieved from STN Database accession no. 131:130065 XP002232044 * abstract * & CHEMICAL COMMUNICATIONS (CAMBRIDGE) (1999), (12), 1095-1096,</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	1,4	<p>C07F1/00 C07F1/08 C07F7/10 C07F5/02 C07F15/00 C23C16/00</p>
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C07F
INCOMPLETE SEARCH			
<p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p style="text-align: center;">see sheet C</p>			
Place of search		Date of completion of the search	Examiner
MUNICH		21 February 2003	Alstanei, A-M
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>_____</p> <p>& : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			

EPO FORM 1503 03.02 (P04007)

European Patent
OfficeINCOMPLETE SEARCH
SHEET CApplication Number
EP 01 10 8053

Claim(s) searched completely:
2,6,12-15,20-23

Claim(s) searched incompletely:
1,3-5,9-11,16-19,24

Reason for the limitation of the search:

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim 1 may be said to define subject-matter for which protection might legitimately be sought (Article 84 EPC). For these reasons, a meaningful search over the whole breadth of the claim 1 is impossible. Consequently, the search has been restricted to the compounds of claim 2 (M and M' are each Cu).



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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ZABURDYAEVA, S. N. ET AL: "Synthesis of eight-membered oxa-.lambda.5-stiba heterocycles from triphenylantimony, dihydroxysilanes, and phenylboronic acid" retrieved from STN Database accession no. 131:257691 XP002232045 * abstract *</p> <p>& RUSSIAN JOURNAL OF GENERAL CHEMISTRY (TRANSLATION OF ZHURNAL OBSHCHEI KHIMII) (1999), 69(1), 82-84 ,</p>	1,4	
	---		TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LIU, FENG-QUAN ET AL: "Syntheses and structure of the first eight-membered fluoro and chloro hafnium siloxane complexes" retrieved from STN Database accession no. 125:58721 XP002232046 * abstract *</p> <p>& ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE (1996), 622(5), 819-822 ,</p>	1,4	

	-/--		

EPO FORM 1503 (03.92) (P04C10)



European Patent
Office

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Application Number
EP 01 10 8053

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MAZZAH, A. ET AL: "Synthesis and structures of boron and germanium containing eight-membered siloxane rings and of a bicycloheptane derivative with silicon, tin, and oxygen as building units of the ring system" retrieved from STN Database accession no. 116:33292 XP002232047 * abstract *</p> <p>& ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE (1991), 604, 93-103 ,</p>	1,4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	<p>--- DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HAOUDI-MAZZAH, AMAL ET AL: "Synthesis and structure of eight-membered titanium and zirconium containing siloxane rings" retrieved from STN Database accession no. 115:71882 XP002232048 * abstract *</p> <p>& ZEITSCHRIFT FUER NATURFORSCHUNG, B: CHEMICAL SCIENCES (1991), 46(5), 587-92 ,</p> <p>--- -/--</p>	1,4	

EPO FORM 1506 03.92 (P04C10)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 01 10 8053

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HAOUDI-MAZZAH, A. ET AL: "Vibrational study of phosphorus, molybdenum and vanadium cyclosiloxane derivatives" Database accession no. 130:153788 XP002232049 * abstract * & JOURNAL OF RAMAN SPECTROSCOPY, vol. 29, no. 12, 1998, pages 1047-1053, ---	1,4	
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HASS, ERNST C. ET AL: "Nonempirical SCF molecular orbital studies on simple zeolite model system" retrieved from STN Database accession no. 97:61334 XP002232050 * abstract * & THEOCHEM (1982), 4(3), 261-72 , ---	1,4	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HAOUDI-MAZZAH, A. ET AL: "Vibrational study of eight-membered zirconium- and boron-containing siloxane rings" Database accession no. 125:142987 XP002232051 * abstract * & JOURNAL OF RAMAN SPECTROSCOPY, vol. 27, no. 6, 1996, pages 451-455, --- -/--	1,4	

EPO FORM 1500 (03.02) (P44C10)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 01 10 8053

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; GOSINK, H.J. ET AL: "Synthesis and Structures of cyclic and acyclic metallasiloxanes of Group 5-7" Database accession no. 121:230994 XP002232052 * abstract * & ORGANOMETALLICS, vol. 13, no. 9, 1994, pages 3420-3426, ---	1,4	
X	US 3 002 986 A (HYDE JAMES F) 3 October 1961 (1961-10-03) * column 3 - column 4; table 1 * ---	1,4	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ALBRECHT, T. ET AL: "Four- and eight-membered metal-containing boron-nitrogen heterocycles. Formation and structures in dependence on the steric requirement of their substituents" retrieved from STN Database accession no. 129:330868 XP002232053 * abstract * & ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE (1998), 624(9), 1514-1518 , --- -/--	1,3	

EPO FORM 1503 (03.92) (P/ALC10)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 01 10 8053

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; GESCHWENTNER, M. ET AL: "Metalla- and phosphaheterocycles with diaminosupermesitylboryl units" retrieved from STN Database accession no. 121:205550 XP002232054 * abstract * & ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE (1994), 620(8), 1403- ,</p>	1,3	
X	<p>--- DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; BARRAU, JACQUES ET AL: "Germanones and germathiones: reactivity with respect to small organic cyclics" retrieved from STN Database accession no. 99:88297 XP002232055 * abstract * & JOURNAL OF ORGANOMETALLIC CHEMISTRY (1983), 246(3), 227-42 ,</p> <p>--- -/--</p>	1	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p>



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 01 10 8053

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; CASTEL, ANNIE ET AL: "Germylene reactivity with respect to ethylene oxide" retrieved from STN Database accession no. 90:38997 XP002232056 * abstract * & COMPTES RENDUS DES SEANCES DE L'ACADEMIE DES SCIENCES, SERIE C: SCIENCES CHIMIQUES (1978), 287(5), 205-8 , ---	1	
X	DATABASE CROSSFIRE BEILSTEIN [Online] Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 4007581(BNR) XP002232057 * abstract * & NOETH, W. ET AL: Z.NATURFORSCH.B ANORG.CHEM.ORG.CHEM., vol. 31, 1976, pages 697-704, ---	1,3	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	DATABASE CROSSFIRE BEILSTEIN [Online] Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 8362214(BNR) XP002232058 * abstract * & HITCHCOCK, P.B. ET AL: J.ORGANOMET.CHEM, vol. 580, no. 2, 1999, pages 386-398, ---	1-3	
A	---	1-3	
	-/--		

EPO FORM 1503 03.02 (P44C10)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 01 10 8053

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,A	US 5 144 049 A (NORMAN JOHN A T ET AL) 1 September 1992 (1992-09-01) * column 4, line 16 - column 7, line 34; example 1 *	1,2,18	
A	US 5 449 799 A (TERFLOTH CHRISTIAN ET AL) 12 September 1995 (1995-09-12) * column 1, line 39 - column 2, line 58 * * column 5, line 66 - column 7, line 68 *	1,2,18	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)

EPO FORM 1503 02.02 (P04C19)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 10 8053

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-02-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3002986	A	03-10-1961	NONE	

US 5144049	A	01-09-1992	US 5085731 A	04-02-1992
			DE 69218478 D1	30-04-1997
			DE 69218478 T2	03-07-1997
			EP 0498269 A2	12-08-1992
			JP 5059551 A	09-03-1993
			JP 6049943 B	29-06-1994
			KR 9411709 B1	23-12-1994
			US 5187300 A	16-02-1993

US 5449799	A	12-09-1995	DE 4222021 A1	05-01-1994
			JP 6088212 A	29-03-1994

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